RESEARCH PROPOSAL

Proposed Title of Work: Electronic Structure of Carbon-based Nanostructures

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Mode of Ph.D.: Full-time Scholar

Registration No.: VB-1260 OF 2013-14

Registration Date: 28.08.2015

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(a) Origin of the research problem

Carbon is one of the most important element in the earth as it plays a crucial role in all living organism and without it we would be lost. The ability of carbon atoms to form cross-linked structure and to exist in three different hybridised state (sp, sp^2 and sp^3) gives rise to a lot of members in its family, among them, some known from ancient time e.g. diamond, graphite. In diamond, each carbon atom is surrounded by four neighboring carbon atoms through covalent linking and are arranged in a face-centered cubic crystal structure. Graphite is a layered materials, which consists of many two-dimensional (2-D) layers of carbon atoms arranged in honeycomb crystal lattice. The scenario is completely changed and a new journey of carbon have been started with the discovery of fullerene (C_{60}) in the year of 1985 by Kroto et al. [1]. This small molecule has not only the interest in fundamental research at low-dimensionality; but also have deep practical importance e.g. fullerene is successfully implemented in organic solar cells. The next representative of carbon comes into the play is carbon nanotube, discovered by Ijima et al. in 1991 [2]. However, the most interesting fact is that three-dimensional (diamond, graphite), zerodimensional (fullerene) and one-dimensional (nanotubes) allotropes of carbon were present, only the two-dimensional form was surprisingly missing, which is discovered very recently (2004) by Geim and Novoselov, known as graphene [3–5]. Electronic band structure of graphene can be obtained by using ab initio simulation packages such as SIESTA [6]. Graphene is a zero gap semiconductor or semi-metal or gapless semiconductor. High electron mobility and long coherence length make graphene a subject of great interest for nanoscale electronic applications. However, a major setback in the development of different graphene-based field is its lack of band gap. To overcome this a straightforward solution is to pattern the graphene sheet into narrow ribbon. Graphene nanoribbons (GNRs) are one dimensional stripes of graphene sheet, in which motion of electrons is allowed in only one direction. Due to particular honeycomb structure of graphene sheet,

are distinct, one is armchair, create armchair GNR two different cutting directions (aGNR) and the other is zig-zag, form zig-zag GNR (zGNR). DFT calculations reveal that even for the 3l+2-GNRs (predicted to be metallic in TB) a small gap opens at k=0 inducing a semiconductor character for all armchair ribbons[7,8]. Nakada *et al* [9] showed that for zigzag ribbons, however, a remarkable new feature arises in the band structure. In zGNR the edge carbon atoms within the same edge are ferromagnetically coupled [10,11] but they are coupled antiferromagnetically across the edge[11,12] result is no magnetic moment as a whole, not only that energy states of up &down spin configuration are degenerate. This is consistent with Lieb's theorem [13] of bipartite system derived from the tight binding Hubbard model. As a result application of zGNR in spintronics device is limited. Several techniques have been used in order to lift the degeneracy of up & down spin states e.g. application of electric field [14] chemical doping [15] and organic functionalization etc. lattice imperfections such as defects present in the crystal may lift the degeneracy of spin states and has great influence on the electronic, optical, and magnetic properties of solid[16].

Recently, a strategy of constructing periodic holes on graphene to form graphene antidot lattices (GALs) has been extensively studied[17,18]. Theoretical calculations have predicted that antidot lattices change the electronic properties of graphene from semimetallic to semiconducting, where the opened gap can be tuned by the size, shape, and symmetry of both the hole and the lattice cell [19]. The induced gap in GALs is approximately proportional to the hole diameter and inversely proportional to the superlattice cell area, so one can achieve a substantial gap value of $\sim$0.2 eV in a unit cell of 10 nm [17]. Accordingly, the transport properties of graphene nanoribbons (GNRs) are modulated by the existence of the antidots[20]. Antidot lattices on graphene also affect the occurrence of flat bands and collective magnetic behavior, and thus may lead to applications in storage media and spintronics[17].

In the recent years, two-dimensional (2D) materials covalent-organic frameworks (COFs) have attraceted severe attention due to their novel electronic, optical, mechanical, catalytic properties for future applications. Covalent organic frameworks (COFs) are a new class of crystals composed entirely

of light chemical elements such as C, N, H, O, and B. Because of the strong covalent bonds in the frameworks, COFs exhibit good thermal stability. In addition to their low gravimetric density and large surface areas, COFs feature versatile electronic behaviors making them ideal candidates for, catalysis[21], chemically separation[22], gas storage[23], and semiconducting and optoelectronic applications[24].

Metal-organic frameworks are the latest members in 2D community with the advantages of both inorganic and organic materials. Metal-organic frameworks are crystalline porus materials composed of metals atoms or cluster linked by various organic ligands. The major advantage of metal-organic frameworks is that their properties and pore size can be controlled by varying the structural components, metal (/metal cluster) and organic linker. The possibility of tuning leads to a remarkable range of electronic, optical and magnetic properties. So, MOFs are emerging with high potential abilities in different fields like catalysis [25], gas storage [26], gas purification and separation [27], sensors [28] etc. Recently, the light harvesting and charge transport properties of MOFs are emerging with great importance for electronic and photonic application components, metal (/metal cluster) and organic linker.

(b) Objective of the work

(1) We are now studying a new type of periodic line defect (LD) within unit cell of perfect zGNR composed of pentagonal and heptagonal sp^2 hybridised carbon rings i.e. 5-7 defect, periodically repeated along edge direction. We have described the zGNR with line defect as N_1-N_2-LD-zGNR, where the widths of the upper and lower ribbon are specified by the no of zigzag chains N_1 & N_2 in the upper and lower ribbon respectively. Depending upon the values of N_1 and N_2 the structure of LD-zGNR becomes symmetric or asymmetric.

Our objective is to study whether a line defect is able to change the magnetic ground state,

electronic properties etc or not. Their stabilities will be determined by virtue of calculation of formation energy. We want to observe is there any variation of electronic properties of LD-zGNR with variation of ribbon width as well as with position of line defect within ribbon for a certain ribbon width? We want to study the effect of electric field and doping on electronic band structures of these systems and also the doping effect using SIESTA code. We also want to study the transport property of these LD-zGNR.

(2) Inspired by the innovative experimental studies by Clough et al. [29] and theoretical studies by Liu et al.[30], we like to study first principle based calculation of the electronic, magnetic and transport properties of a 2D bis(dithioline) based MOF, MBHT where M = Co, Fe, Mn, Cr using SIESTA Code. Then we like to investigate the gas (CO) adsorption properties of these bis(ditholine) based metal-organic framework in both single and double side of the planar 2D sheet of MOF(as because of unsaturation of the metal coordination no in square planar MOF) and to observe the effect of these adsorption on electronic properties and to find whether it is applicable for sensor or not.

(3) Recently, Li *et al.*[31] have synthesized a new 2D azine-linked covalent organic framework, ACOF-1 by condensation of hydrazine hydrate and 1,3,5-triformylbenzene under solvothermal conditions. This is constructed by a donor (D) part azine linkage and an acceptor (A) unit 1,3,5-triformylbenzene. The donor–acceptor heterojunction is an important key structure in current technologies, including light-emitting diodes, transistors, and photovoltaics, because it controls the charge dynamics in the devices. In this context, we want to carry out a theoretical study using density functional theory (DFT) calculations on the electronic properties of ACOF-1. We would like to investigate its photovolatic application by charge separation between donor-acceptor moiety. We are also interested to show how to tune its charge separation property to charge transfer by suitable pairing of different donor and acceptor moiety for application in optoelectronic devices. Mainly, COFs are spin-unpolarized so its application

in spintronic devices are restricted, hence we are interested to find out the way of generating spin-polarization in ACOF-1 and want to systematically calculate its spin related electronic and magnetic properties. We will also design two composite system of ACOF-1 and fullerene. One by inserting fullerene within the pore of ACOF-1 or by linking fullerene with ACOF-1 by ester linkage. Hence, we would like to find out whether there is any spatially charge separation between ACOF-1 and fullerene, as fullerene is a good acceptor unit. This may rise the ACOF-1 composite system as a good candidate for photovoltaic application.

(c) Methodology

The ultimate goal in Solid state Physics is to solve Schrödinger equation-

$$\hat{H}\Psi(r;R) = E\Psi(r;R) \qquad \ldots(1)$$

Where,

$$H = \underbrace{-\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2}_{T_e} \underbrace{-\sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2}_{T_N} \underbrace{-\sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}}}_{V_{eN}} + \underbrace{\sum_{i=1}^{N-1}\sum_{j>i}^{N}\frac{1}{r_{ij}}}_{V_{ee}} + \underbrace{\sum_{A=1}^{M-1}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}}}_{V_{NN}} \quad (1) \qquad \ldots(2)$$

Where

$$\nabla_i^2 = \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right),$$

M_A = Mass of nucleus A
Z_A = Atomic number of nucleus A
T_e = Kinetic energy operator for the electron
T_N = Kinetic energy operator for the nuclei
V_{eN} = Operator for potential energy of the attractions between the electrons and the nuclei
V_{ee} = Potential energy of repulsions between the electrons
V_{NN} = Operator considering potential energy of repulsions between the nuclei A and B

Equation (1) is impossible to solve in practice for the above Hamiltonian due to presence of cross terms r_{iA}, $r_{ij,}$ R_{AB}. Hence approximation is required.

Born-Oppenheimer approximation:

The nuclei are much heavier than electrons (m_{proton}=1836m_e), hence they move much more slowly and can be considered frozen in a single arrangement (molecular conformation). So the electrons can respond almost instantaneously to any change in the nuclear position. Thus, the electrons in a molecule are moving in the field of fixed nuclei. So the term T_N can be neglected and the molecular Hamiltonian becomes-

$$H = \underbrace{-\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2}_{T_e} \underbrace{-\sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2}_{T_N} \underbrace{-\sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}}}_{V_{eN}} + \underbrace{\sum_{i=1}^{N-1}\sum_{j>i}^{N}\frac{1}{r_{ij}}}_{V_{ee}} + \underbrace{\sum_{A=1}^{M-1}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}}}_{V_{NN}}$$

neglected

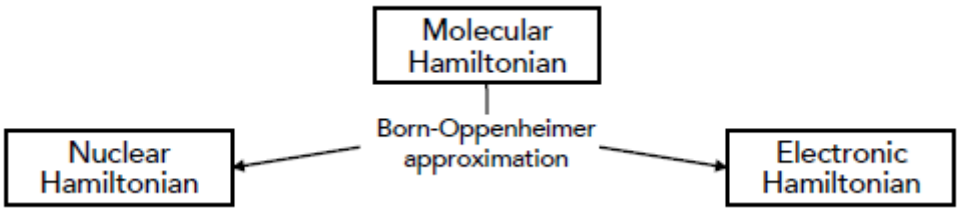
constant term

……(3)

The Born-Oppenheimer approximation allows the total wave function to be written as product of electronic and nuclear wave function as follows

$$\Psi(r, R) = \Psi_e(r;R) \bullet \chi_N(R)$$

Ψ_e is parametrically dependent on position of nucleus(R).



Electronic Hamiltonian describes the motion of N electrons in the field of the M fixed point charges (nuclei).

$\hat{H}_e$

$$H_e(R) = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N-1} \sum_{j>i}^{N} \frac{1}{r_{ij}} \qquad (2)$$

……(4)

Electronic Schrödinger equation:

$$\hat{H}_e \Psi(r;R) = E_e \Psi(r;R) \qquad \text{…….(5)}$$

Solution of equation (5) gives the electronic energy E_e and the wave function $\Psi(r;R)$ for a particular value of R.

Finally total energy can be obtained by adding internuclear repulsion energy (V_{NN}) to electronic energy.

Total energy:

$$E_{tot}^{pot}(R) = E_e + \sum_{A=1}^{M-1} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}$$

……(6)

Equation (5) can be solved with the help of Density Functional Theory (DFT). The spin-polarised DFT is employed in our electronic structure calculations as implemented in SIESTA code [32]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof exchange-correlation functional [33] is adopted with the norm-conserving pseudopotentials and the double zeta plus polarisation basis set.

(d) Future Prospect

In this research work we will try to explore some of the interesting aspects of carbon-based nanostructures. Carbon may exists with other atoms like B, N and transition metals (COF and MOF), which may spread the empire of carbon in material science. Our study will open up few possibilties of understanding to experimentalist and further exploration of designing other 2D COF, MOF, porous graphene and other carbon-based materials. These COF materials may find their application in photovoltaic and optoelectronic device fabrication. MOFs may prompt the exprimentalist for spintronic device fabrication.

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